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The thermoluminescence intensity of x-irradiated spectroscopically pure single KCl crystals has been measured over a temperature range from 25°C to 300°C. The effects of heat treatment and optical bleaching on the glow curves were analyzed. It was found that heat treatment increased the low temperature peaks and decreased the highest temperature peak, whereas, optical bleaching produced a single high temperature glow peak. The thermoluminescence emission spectrum was analyzed and found to consist of three different energies. An unsuccessful attempt was made to calculate the activation energy for color center electrons using the Halperin model to compare with values obtained by the initial rise method. It was proposed that these attempts were unsuccessful because a single glow peak in these KCl crystals was due to more than one trap depth. Optical absorption measurements were made which indicated that F centers were present; therefore, the glow peaks were attributed to F center destruction.

ANALYSIS OF COLOR CENTER THERMOLUMINESCENCE IN KCl CRYSTALS

by

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CHAPTER I

BACKGROUND

It has been known for almost two hundred years that some elements, usually transparent, are sometimes discovered in nature to exhibit a particular color of the visible spectrum. As early as 1800 researchers reported that these colored materials could be bleached out and re-colored by using electric sparks, ultraviolet light or other high energy radiation. Studies of coloring became more systematic after 1896 when Goldstein found that these materials could be colored by irradiation.

One of the earlier researchers, Pohl in 1937, coined the name "color centers" for coloring in solids due in some way to electrons. Since then many models of color centers have been proposed. However, experiments which confirm these models have been very difficult to devise. With the increasing interest in solid state physics and studies of imperfections in crystalline structure, physicists began to believe that color centers were related to imperfections in the solids.[1]

Color centers of many different types are known to exist in crystals. In 1946 Seitz[2] proposed models of some of the color centers occuring in the alkali halide crystals. Since then much research has been done to test the validity of these models.

The alkali halide compounds are some of the simplest in crystalline structure and can easily be obtained in a relatively pure form. Also, many of their properties are well understood. Therefore, it seems natural to choose these compounds to study. There are several types of lattice

defects in the alkali halide crystals that absorb visible light and hence are called color centers.

The simplest type and probably the most well known type of color center in these crystals is the F center. The origin of the term "F center" comes from the German word Farbe, meaning color. The F center is analogous to the hydrogen atom in atomic physics because much can be learned about the nature of color centers by understanding the F center. The first successful model of the F center was proposed in 1937 by de Boer and with some modification has withstood many experimental and theoretical investigations. This model consists of an electron trapped or associated with a negative ion vacancy in the crystal. The following figure from Kittel[3] shows the electron charge distribution of an electron trapped in a negative ion vacancy.

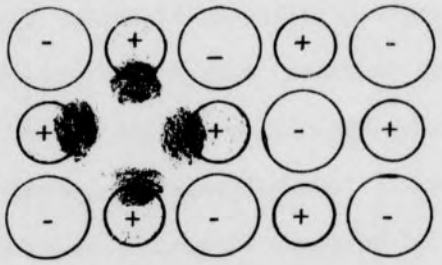

Figure 1: De Boer model of the F center.

When a colored alkali halide crystal containing F centers is exposed to white light a broad absorption band in the visible region is observed. The spectral location of this band depends upon the lattice constant of the particular alkali halide being irradiated. This absorption band is known as the F band and is temperature dependent becoming narrower with the peak shifting to shorter wavelengths as the temperature of the crystal is decreased. At high temperatures the band width varies as the square root of the absolute temperature and as the crystal is cooled the band width approaches a width of a few tenths of an electron volt of energy. Optical absorption, a technique of studying F centers which will be discussed later, is a quantitative analysis of this absorption band.[4]

Just as the hydrogen atom, the F center has excited states. Figure 2 is an energy level diagram of an F center and its excited states as proposed by Markham.[5] The F center is an electron trapped between the conduction and valance band of the crystal. Another interesting point is that the F center absorbs light in the visible region and emits light in the infrared region. This happens because the excitation time of the electron absorbing visible light is instantaneous compared to the period of lattice vibrations (Franck-Condon Principle). The lattice adjusts to the new energy of the electron so that when the electron falls back to the ground state the trap is not as deep, hence infrared light is emitted (Stokes' Shift). A more detailed discussion can be found in Brown.[6] Note that this diagram shows the thermal broadening of the energy states of the F center.

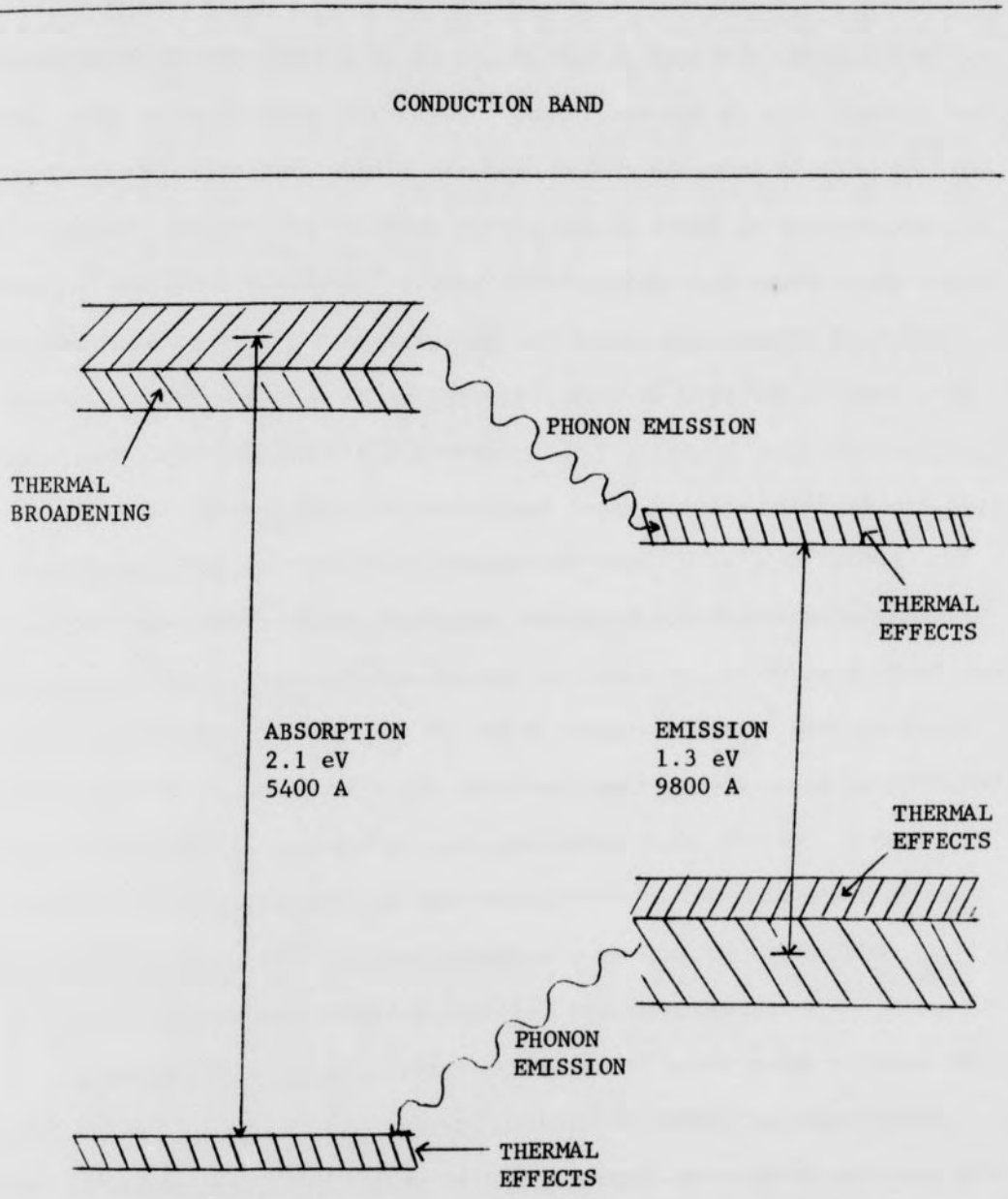

Figure 2: Energy level diagram for an F center. (KC1)

Some other types of color centers known to exist in the alkali halide crystals are the F', M, R, R_1, N, and F_A centers. Models for these color centers other than the F' center are not as well established as that of the F center. Seitz proposed models for most of them in 1946 and a general discussion of these models can be found in Compton and Schulman[4] and also in Brown.[6] These color centers are essentially aggregates of F centers. They absorb light of longer wavelengths than the F center and are unstable at temperatures from 23°C to 110°C above room temperature decaying back to F centers.

In addition to the above mentioned color centers which absorb light of wavelengths longer than the F center and seem to be some arrangement of trapped electrons, there are color centers which absorb wavelengths shorter than the F band. These absorption bands are known as V bands and are associated with V_1, V_2, V_3, V_k and H centers. Seitz[2] also proposed models for these color centers in 1946 but their models are not confirmed and result mostly from electron spin resonance measurements. A more thorough discussion as well as some models can be found in Compton and Schulman[7] and in Brown.[6] These centers are thought to be various combinations of trapped holes at positive ion vacancies.

Just as there are many different types of color centers found in the alkali halides there are several methods of producing these color centers in these crystals. Some of the important methods of coloring are additive coloration, electrolytic coloration, x-irradiation, or almost any other high energy radiation such as neutrons or high energy electrons. A detailed discussion of these different coloration methods can be found in Compton and Schulman.[8]

Additive coloration consists of heating the crystal under high pressure in the presence of either the halogen or alkali metal vapor then cooling it rapidly, thus freezing the color centers in. Unless done very carefully this method will also introduce impurities because of the high temperature, thus V centers may form as well as F centers. Electrolytic coloration consists of introducing point electrodes into the crystal and heating it to a high temperature in the presence of an electric field. F centers will collect around the cathode and V centers around the anode creating colored zones which are colorless where they intersect.

Probably the most useful method of coloring crystals is by x-irradiation. This method has a distinct advantage over the other methods in that it can be done at any temperature from liquid helium temperatures to well above room temperature. Ionizing radiation can be produced by almost any source. The energies of the ionizing radiation range from ultra-violet light of about 10 electron volts, to x-rays from 10 to 60 thousand electron volts, to gamma rays of a few million electron volts, to high energy particles such as electrons, protons, or neutrons of several hundred million electron volts. Soft x-rays color the crystal most intensely at the surface with an approximate exponential decrease of coloration inside the crystal. High energy gamma rays color the crystal deeper. However, shielding problems result because of the high intensity radiation sources necessary to produce significant coloration. High energy charged particles such as protons have short ranges within the crystal giving rise to local heating in regions of the crystal which create problems for low temperature x-irradiation.

The amount of coloration of a crystal is proportional to x-ray exposure time. The amount of coloration for a given exposure time depends upon the particular alkali halide being x-rayed. Color centers of one type may be converted to another type by more irradiation or by exposure to bright light usually of the wavelength which these centers absorb.

One of the most useful and probably best understood methods of studying color centers is optical absorption. Optical absorption measurements are made by taking the ratio of light intensity of a given wavelength absorbed by a colored crystal to the intensity a normal crystal absorbs, and plotting a graph of percent absorption versus wavelength. These absorption measurements are made with a double beam spectrophotometer, an instrument which exposes both crystals to the same intensity of light of a given wavelength simultaneously. The wavelengths used range from 30000 to 1800 angstroms depending on the quality of instrument used. Optical absorption measurements are used to identify the type of color center present in the crystal by its characteristic absorption band.

Using an empirical relation known as Smakula's equation, the density of F centers in a crystal can be calculated using the width of the F band and oscillator strength of the F center. Smakula's equation can be put in the form

$$Nf = 1.29 \times 10^{17} \frac{n}{(n^2 + 2)^2} \alpha_{max} W_{\frac{1}{2}} , \qquad (1)$$

where,

N = number of F centers per cm^3,

f = oscillator strength (a number from .8 to .9),

$W_{\frac{1}{2}}$ = half width of F band in electron volts,

α_{max} = maximum absorption coefficient in cm^{-1},

n = index of refraction of crystal,

$$\alpha_{max} = \frac{\log_{10} \frac{I_o}{I}}{X} = \frac{(O.D.)}{X} ,$$

(O.D.) = optical density,

I_o = intensity of light through reference crystal,

I = intensity of light through colored crystal at the peak, and

X = crystal thickness in cm.

The use of Smakula's equation is open to question because it uses a gaussian curve and the actual absorption curve is Lorentzian. However it is a good empirical approximation if reliable estimates of the oscillator strength are available.[4, 6]

Some other methods of studying color centers in alkali halide crystals are luminescence, photoconducitivity, electron spin resonance and thermoluminescence. Luminescence is a quantitative study of the emission spectra of the color centers by measuring the total emission spectrum for a given wavelength of exciting light. Much can be learned about the symmetry of F centers using polarized light, optical absorption techniques and luminescence.

Colored crystals containing F centers will conduct electric current when stimulated by green light. This current is temperature dependent and consists of primary and secondary photo current. Primary current is dominant from $-150^{\circ}C$ to $-70^{\circ}C$, depending upon the type of alkali halide

crystal, and rises and falls instantaneously as the light is turned off. The secondary photo current appears at temperatures from -75°C to 25°C, depending on the kind of alkali halide crystal, rising and falling more slowly as the light is turned on and off. These currents are attributed to F centers because at low temperatures the electrons are freed and retrapped quickly compared to the response time of the measuring instrument whereas at higher temperatures the electrons are free to move around for large times compared to instrument response time before being retrapped due to thermal agitation. A more comprehensive discussion of photoconductivity can be found in Seitz's[2] article.

Electron spin resonance has been the most reliable method of determining a specific model of the F center. The unpaired electron or hole has a net spin giving rise to an energy splitting in the presence of a magnetic field and the resonance energy between levels can be measured.

As mentioned earlier color centers are formed when crystals are bombarded with x-rays. Some of the electrons (or holes) are freed to wander through the crystal until trapped where they would not normally be. When these crystals are heated to a sufficiently high temperature the electrons (or holes) are released by thermal agitation and either get retrapped or recombine destroying the color center and bleaching the crystal. The phenomenon of thermoluminescence arises in the process of recombination of electrons and holes after thermal release. The resulting emission of light reaches a maximum, then decreases to zero as the temperature of the crystal increases. "Glow curves" are obtained by recording the light intensity as a function of temperature at a constant heating rate. A

CHAPTER II

THERMOLUMINESCENCE THEORY

Thermoluminescence is one of several techniques of studying color centers in crystals. Several authors have developed theoretical models of the kinematics of thermoluminescence, all of which reduce to essentially the same results within the proper limits. However, experimental varification of these theories has not enjoyed the same degree of success as has the de Boer model of the F center. In the first chapter, thermoluminescence was described as the thermal release of trapped electrons and their recombination with trapped holes, emitting light in the process.

The exact method by which the electrons are released when the crystal is heated is not understood. It is generally believed that the electrons are removed from their traps by thermal agitation into the conduction band or into an excited state very near the conduction band. Regardless of which process actually occurs, two things are most likely to happen. Either the electron will be retrapped if it is in the conduction band, de-excited if it is in an excited state and the F center is not destroyed, or the electron will recombine with a trapped hole between the conduction and valence bands or within the valence band and the F center will be destroyed. In the model to be presented radiationless transitions are assumed unless the F center is destroyed; therefore, it is the latter process that is responsible for the light given off during thermoluminescence. It seems

given glow curve may have one or more peaks and these peaks may be either separate or overlapping. The different peak temperatures are commonly attributed to color centers of different trapped depths. The shape and size of a glow curve is a function of radiation time. A correlation between the temperatures at which thermoluminescence occurs and that at which a particular optical absorption band bleaches out may yield valuable information about a particular color center.[8]

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natural that any mathematical model of the kinematics of thermoluminescence must consider the relative importance of these competing processes.

Randall and Wilkins[9] were the first to derive an expression for the thermoluminescence of a glow curve. They assumed that the electrons were trapped with some activation energy E below the conduction band, that the electrons had a Maxwellian energy distribution and that retrapping or de-excitation was not significant. Jain and Mehendru[10] concluded experimentally that retrapping was not significant in the glow curves of highly pure NaCl and KCl crystals. Halperin and Braner[11] and also Kelly and Laubitz[12] have presented more general mathematical treatments of glow curves. In both papers expressions are derived for the thermoluminescence process when retrapping is significant. Also, these equations reduce to those of Randall and Wilkins when retrapping is not significant.

The remainder of this chapter will be a development of the Halperin model and the modifications used to explain some of the experimental results. The general treatment consists of two sub-models: The first assumes that the electron goes to an excited state before recombination and the second assumes that the electron goes to the conduction band before recombination. Both sub-models take into account the relative significance of retrapping and yield a rather simple expression for the activation energy. The procedure will be to derive expressions for the activation energy for the excited state model and its two limiting cases. Only the kinematic equations for the excited state model are presented because as was noted by Halperin and Braner[11] the only effect of the electron going to the conduction

band is to add a samll correction to expressions for the activation energies of the excited state model.

An energy level diagram for the Halperin model is shown in Figure 3. This model assumes that there exist certain discrete energy levels between the conduction and valence bands in which electrons and holes are trapped, with the hole traps being nearer the valence band.

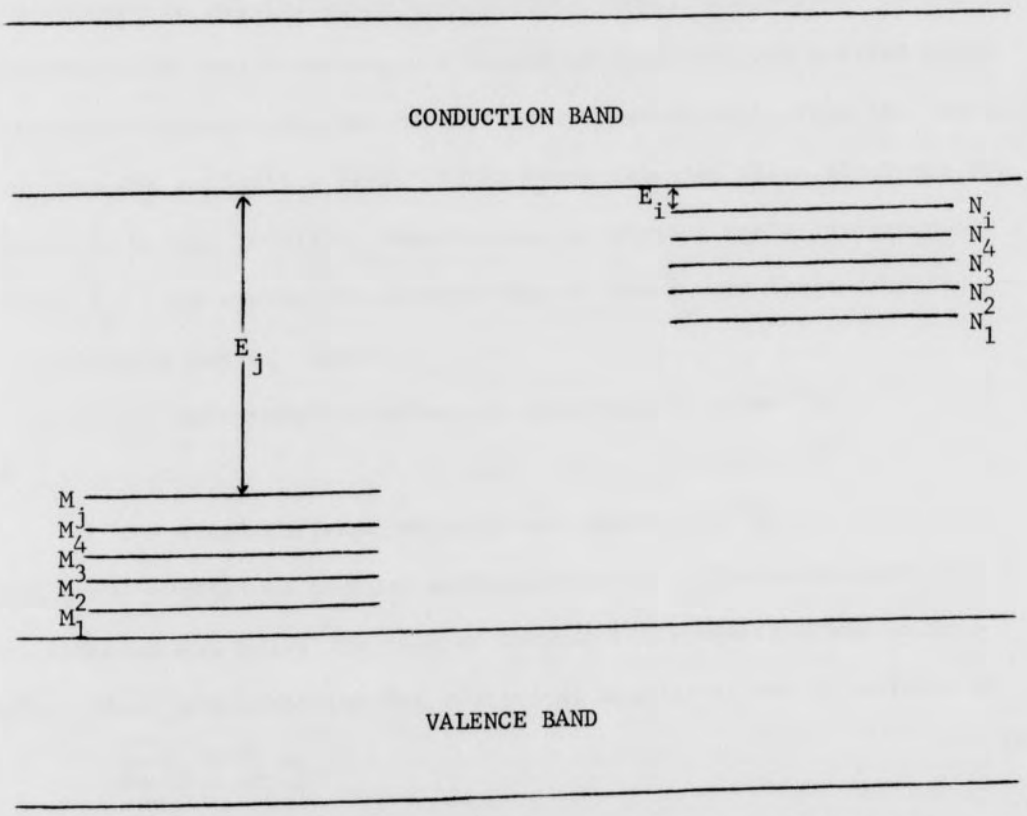


Figure 3: An energy level diagram of Halperin model showing electron traps and hole traps.

In Figure 3,

E_i = activation energy of electron traps below the conduction band,

N_i = number of electron traps per cm^3 of energy E_i,

E_j = energy of hole traps below the conduction band,

and

M_j = number of hole traps per cm^3 of energy E_j.

The term empty luminescence centers maybe considered analogous to trapped hole centers in the following discussions. Empty luminescence centers (trapped holes) and F centers are formed as electrons are excited by x-irradiation either from luminescence centers or directly from the valence band into the conduction band. After being released these electrons are trapped in energy levels N_i simultaneously trapping empty luminescence centers M_j. The assumption is made that E_i and E_j are large compared to kT in electron volts. Where

k = Boltzmann's constant in electron volts per ^oK

and

T = absolute temperature of the crystal in ^oK.

Under these conditions thermal agitation can be neglected so that most of the electrons and holes are trapped between the conduction and valence bands. Also, the condition for electrical neutrality may be written as

$$\sum n_i = \sum m_j. \tag{2}$$

Where

n_i = number of filled electron traps per cm^3

and

m_j = number of filled hole traps per cm^3.

This means that the number of trapped holes equals the number of trapped electrons at any time. Because thermoluminescence occurs when electrons or holes are liberated they are mathematically equivalent. In the following discussion it is assumed that electrons are undergoing transitions and hence F center destruction is responsible for thermoluminescence.

The Halperin model assumes that in the small energy range of a single glow peak only one electron trap of activation energy E and concentration N releases electrons which recombine with a single hole level of concentration M giving rise to a single isolated glow curve. Since other hole levels may be present in the crystal the condition for electrical neutrality becomes

$$\Delta m = \Delta n \tag{3}$$

or

$$m_o - m = n_o - n. \tag{4}$$

In equation (4),

m_o = number of trapped holes initially present in the crystal,

n_o = number of trapped electrons initially present in the crystal,

m = number of trapped holes after some time t,

and

n = number of trapped electrons after time t.

Figure 4 is a diagram of the excited state model of an F center giving rise to a single isolated glow peak. In Figure 4,

n = number of one kind of F center in the ground state,

n_e = number of F centers in the first excited state,

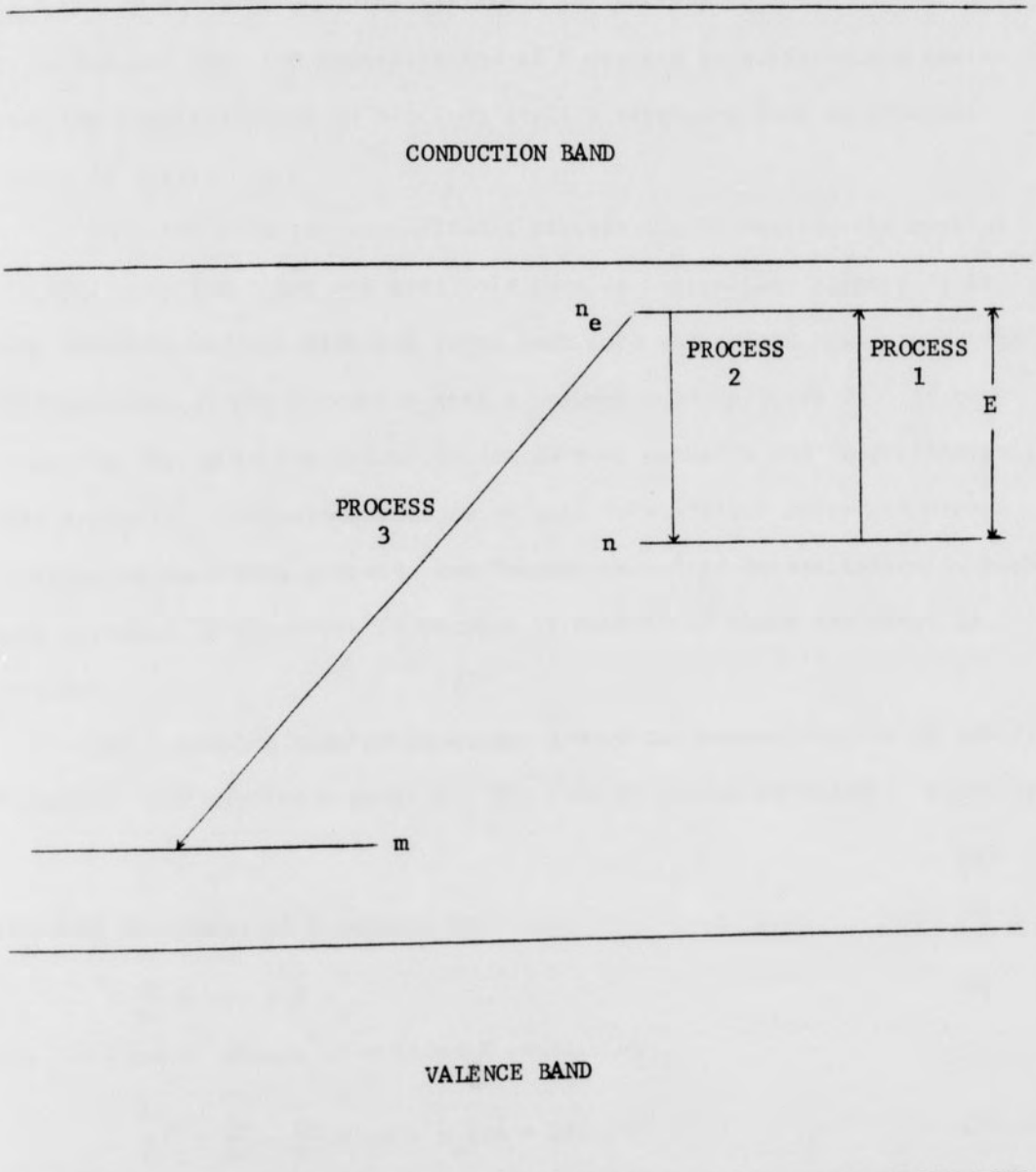


Figure 4: Halperin model of the excited state F center.

and

m = number of holes available for retrapping.

It is assumed that the concentration of F centers is sufficiently small that the possibility of an electron getting retrapped into an adjacent center is negligible.

When the F center is excited (process 1), by heating the crystal, if relatively few holes are available then de-excitation (process 2) is most probable and the electron drops back into the ground state or though less probable it may recombine with a trapped hole (process 3). If many holes are available the recombination is most probable and de-excitation is less probable. Thermoluminescence is said to be "first order" if recombination is much more probable and "second order" if de-excitation is much more probable or somewhere in between if neither of these processes is dominant.

The following kinetic equations govern the concentrations of holes, F centers, and excited F centers. The rate of change of holes is given by

$$\frac{dm}{dt} = -Amn_e, \tag{5}$$

the rate of change of F centers by

$$\frac{dn}{dt} = -\gamma n + S\, n_e, \tag{6}$$

and the rate of change of excited F centers by

$$\frac{dn_e}{dt} \equiv \frac{dm}{dt} - \frac{dn}{dt} = \gamma n - n_e(mA + S). \tag{7}$$

Where

A = the probability per unit time for recombination,

S = the probability per unit time for de-excitation,

and

γ = the probability per unit time for excitation.

The excitation probability per unit time is given by

$$\gamma = S \exp[-E/kT]. \tag{8}$$

Assuming no net accumulation of electrons in the excited state, equation (7) is equal to zero. Setting equation (7) equal to zero and using the conditions for crystal neutrality, $n_e = m - n$, yields the following expression for the number of excited F centers

$$n_e = \frac{\gamma m}{\gamma + S + mA} . \tag{9}$$

Substituting this expression for the number of excited F centers into equation (5) yields

$$\frac{dm}{dt} = - \frac{A\gamma m^2}{S + mA} . \tag{10}$$

for the recombination rate, where it has been assumed that

$$\frac{E}{kT} \gg 1, \tag{11}$$

which is typically the case in actual experiments.

It is reasonable to assume that the thermoluminescence intensity is porportional to the recombination rate. Then the equation for the thermoluminescence intensity is

$$L \equiv -C \frac{dm}{dt} = \frac{C\gamma m}{1 + \frac{S}{mA}} \tag{12}$$

where,

L = the light intensity in arbitrary units,

and

C = a constant depending upon the geometry of the apparatus and the quantum efficiency of the photomultiplier tube.

Using the condition that the glow curve have a peak equation (12) can be differentiated to get

$$m\left(1 + \frac{S}{mA}\right)\frac{d\gamma}{dT} + \gamma\left(1 + \frac{2S}{mA}\right)\frac{dm}{dT} = 0. \tag{13}$$

Substituting

$$\frac{d\gamma}{dT} = \frac{E}{kT^2}\gamma \tag{14}$$

and

$$\frac{dm}{dt} = -\frac{\gamma m}{\beta\left(1 + \frac{S}{mA}\right)} \tag{15}$$

into equation (13) and rearranging yields

$$\left(1 + \frac{S}{mA}\right)^2 \frac{E\beta}{kT^2} = \gamma\left(1 + \frac{2S}{mA}\right), \tag{16}$$

where

β = the heating rate, $\frac{dT}{dt}$, assumed constant.

Denoting quantities at the peak by the subscript p and rearranging equation (16) gives

$$\frac{E}{kT_p^2} = \left[\frac{1 + \frac{2S}{m_p A}}{1 + \frac{S}{m_p A}}\right]\left[\frac{\gamma_p}{\beta\left(1 + \frac{S}{m_p A}\right)}\right]. \tag{17}$$

And from equation (12) the light intensity at the glow peak is

$$L_p = \frac{C\gamma_p m_p}{1 + \frac{S}{m_p A}}. \tag{18}$$

The area under the glow curve from the initial temperature T_o of the crystal to some arbitrary temperature T is given by

$$J \equiv \int_{T_o}^{T} L \, dT = C\beta \int_{m}^{m_o} dm = C\beta (m_o - m), \tag{19}$$

where

J = the area under the glow curve,

m_o = concentration of trapped holes before heating,

and

m = concentration of trapped holes at temperature T.

Using equation (19) and the fact that $m = 0$ at $T = \infty$ (from the conditions for crystal neutrality) yields

$$J_\infty = C\beta m_o \tag{20}$$

and

$$J_p = C\beta m_p \, . \tag{21}$$

Where

J_∞ = total area under the glow curve

and

J_p = area under the glow curve beyond the peak.

The ratio of the intensity at the glow peak to the area beyond the peak is given by

$$R \equiv \frac{L_p}{J_p} = \frac{\gamma_p}{\beta\left(1 + \frac{S}{m_p A}\right)} \, . \tag{22}$$

Using this result, equation (17) reduces to

$$\frac{E}{kT_p^2} = KR \tag{23}$$

where

$$K \equiv \frac{1 + \frac{2S}{m_p A}}{1 + \frac{S}{m_p A}} . \tag{24}$$

Equation (23) can be used to determine the activation energy if T_p, R, and K are known. Since R and T_p are directly measurable from the glow curve a way must be found to determine K from the glow curve.

An equation for K in terms of quantities determined directly from the glow curve can be obtained in the following way. Equation (10) can be integrated directly, by changing variables from time to temperature, to yield

$$\frac{m_p}{m_o} = \exp\left[\frac{S}{m_p A}\left(1 - \frac{m_p}{m_o}\right) + \frac{SE}{\beta k} \int_{u_o}^{u_p} u^{-2} \exp[-u]\, du \right] \tag{25}$$

where

$$u = \frac{E}{kT} . \tag{26}$$

The integral in equation (25) can be converted to a standard form by first writing it as the difference of two integrals:

$$\int_{u_o}^{u_p} u^{-2} \exp[-u]\, du = -\left[\int_{u_p}^{\infty} u^{-2} \exp[-u]\, du - \int_{u_o}^{\infty} u^{-2} \exp[-u] du \right] . \tag{27}$$

Upon making a change of variables, $u = u_p z$, equation (27) can be written as

$$\int_{u_o}^{u_p} u^{-2} \exp[-u]\, du = \frac{\mathcal{E}_2(u_o)}{u_o} - \frac{\mathcal{E}_2(u_p)}{u_p}, \tag{28}$$

where

$$\mathcal{E}_2(x) \equiv \int_1^{\infty} z^{-2} \exp[-xz]\, dz \tag{29}$$

is the so called exponential integral of the second kind and has been tabulated by Abramowitz and Stegun.[13] Using (28) equation (25) becomes

$$\frac{m_p}{m_o} = \exp\left[\frac{S}{m_p A}\left(1 - \frac{m_p}{m_o}\right) + \frac{SE}{\beta k}\left\{\frac{\mathcal{E}_2(u_o)}{u_o} - \frac{\mathcal{E}_2(u_p)}{u_p}\right\}\right], \tag{30}$$

Defining the quantity r as the ratio of the area under the glow curve and using equations (20), (21), (24), and (30) gives

$$r \equiv \frac{J_p}{J_\infty} = \frac{m_p}{m_o} = \exp\left[\left(\frac{K - 1}{2 - K}\right)(1-r) + \frac{SE}{\beta k}\left\{\frac{\mathcal{E}_2(u_o)}{u_o} - \frac{\mathcal{E}_2(u_p)}{u_p}\right\}\right]. \tag{31}$$

This is an exact expression for r which can be simplified to get

$$\ell n\ r = (1-r)\left(\frac{K - 1}{2 - K}\right) - \frac{1 + Q_p}{K(2-K)} \quad . \tag{32}$$

Using the series expansion from Stegun[13] for $\mathcal{E}_2(u)$

$$\frac{\mathcal{E}_2(u)}{u} = u^{-2} \exp[-u]\ (1-Q), \tag{33}$$

$$Q = \left(\frac{2}{u} - \frac{6}{u^2} + \ldots\ldots\right), \tag{34}$$

the approximate expression for Q_p is

$$Q_p = \frac{2}{u_p} \quad . \tag{35}$$

Equation (32) is an approximate expression for K in terms of quantities measurable from the graph. This equation is as accurate as the data that can be taken from the glow curve because

$$\frac{\mathcal{E}_2(u_o)}{u_o} \ll \frac{\mathcal{E}_2(u_p)}{u_p} \tag{36}$$

and

$$u_p \gg 1 \quad . \tag{37}$$

It is possible to calculate the activation energy of a given glow curve by first solving equation (32) for K in terms of r and T_p which are measured from the glow curve, then solve equation (23) in terms of K, R, and T_p.

The quantity K can be thought of as an order parameter since an examination of equation (24) will show that

$$K = 2 \tag{38}$$

when $S \gg m_p A$ and

$$K = 1 \tag{39}$$

when $S \ll m_p A$. These are the conditions for second order and first order respectively. Also, the expressions for the activation energy in the first and second order limits are, respectively,

$$E = kRT_p^2 \tag{40}$$

and

$$E = 2kRT_p^2 \ . \tag{41}$$

Equation (40) can be obtained from the theory of Randall and Wilkins[9] and also from that of Kelly and Laubitz[12] in the limits that retrapping is not significant.

A method of finding the activation energy which is independent of all of the theories mentioned is that of initial rise. The thermoluminescence intensity just as the curve begins to rise is given by

$$L = C \exp[-E/kT]. \tag{42}$$

The activation energy is found by plotting a graph of the natural log of the intensity versus 1/T and finding the slope of the best straight line

which fits the data. The initial rise method has the advantage of being able to determine the activation energy without knowing the order of the process. However, this method has two disadvantages: First, the curve must have a clean leading edge and, second, the activation energy has a large uncertainty as a result of a large uncertainty in the intensity as the glow curve is just beginning to rise. The initial rise method is commonly used as a check on the other methods or for an estimation of the activation energy. Its accuracy can be improved experimentally.

CHAPTER III

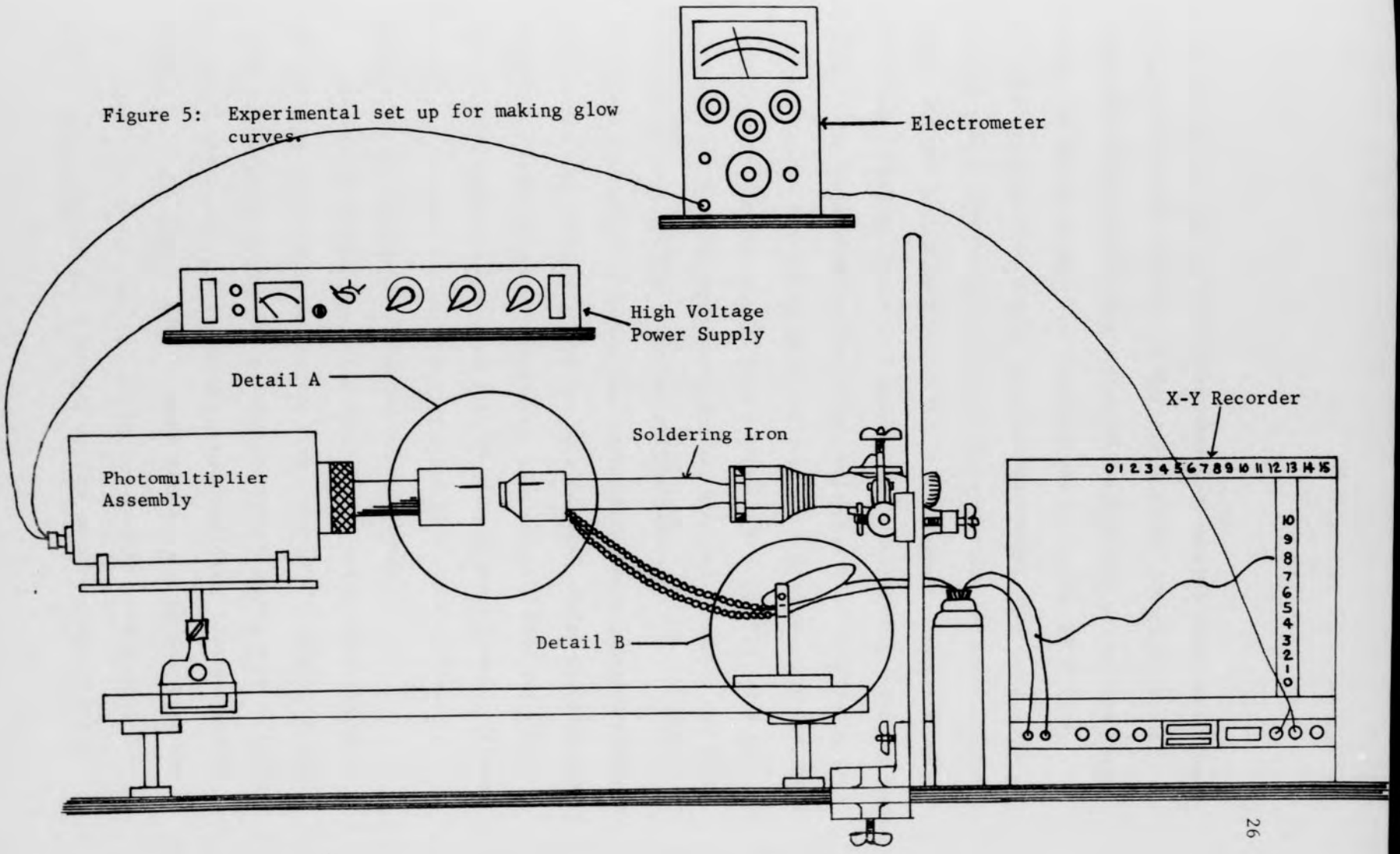
EXPERIMENTAL CONSIDERATIONS

Experimental Equipment

The experimental apparatus used to make the glow curves is shown in Figure 5. Using this apparatus, typical glow curves were made in the following way. The crystal was placed in position on the tip of the soldering iron which was then mounted in front of the photomultiplier. The photo current was monitored visually with an electrometer and recorded on the y-axis of an x-y recorder. The temperature of the crystal was measured using a standard copper constantan thermocouple with the reference junctions in an ice bath. It was calibrated in millivolts using a calibration chart produced by the National Bureau of Standards. The temperature signal was recorded in millivolts on the x-axis of the x-y recorder and also fed into a model G-14 Varian strip-chart recorder to determine the heating rate of the crystal.

The crystals were colored using a Phillips Norelco model 12010120 water cooled x-ray diffraction unit with a copper targer, anode to cathode voltage of 35 kV and a current range from 10 to 20 mA. The x-rays from the copper target consisted of a K_{α} doublet of approximately 1.54 angstroms and a less intense K_{β} line of 1.39 angstroms. The use of a nickel filter increased the K_{α} to K_{β} intensity ratio to approximately 500 and also reduced the low energy x-rays hitting the crystal. Aluminum foil of approximately .02 millimeters thickness was used to cover the tip of the soldering iron during x-irradiation, filtering out very low energy

Figure 5: Experimental set up for making glow curves.



x-rays and protecting the colored crystal from outside light until the glow curve was made. The use of the nickel filter and aluminum foil changed the shape of some glow curves indicating that the surface coloration by low energy x-rays was being reduced by the use of filters.

The crystals were heated at a uniform heating rate using a 200 watt soldering iron. The thermoluminescence intensity was detected using an RCA 6199 end window photomultiplier having S-11 spectral response and a gain of approximately 600,000. A model 600A Keithly electrometer was used to monitor the thermoluminescence signal which was then recorded on the y-axis of a model 2000 Omnigraphic x-y recorder. A model 2K-10 D.C. high voltage regulated power supply, with a range from 1 to 2012 volts and 0 to 10 mA from Power Designs Incorporated, was used to supply the anode to cathode voltage of 1000 volts for the phototube.

For purposes of measuring the thermoluminescence emission spectrum the phototube was cooled with dry ice in a PM 101-2 cooled photomultiplier assembly from Electro Optics Associates. The emission band was swept using an Oriel Optics Corporation F-11-20 scanning monochromator driven with a 4 r.p.m. motor and using a slit width of 1 to .2 millimeters depending on the intensity of the thermoluminescence.

Optical absorption measurements were made using a Perkin-Elmer model 124 dual beam spectrophotometer with a wavelength range from 8000 to 1900 angstroms which fed the percent absorption signal into a Perkin-Elmer model 165 recorder. The crystals were optically bleached using F band green light from a model 33-86-07 Bausch and Lomb monochromator.

Both the x-y recorder and the Varian recorder were checked for linearity using a Heath model EUW-16A voltage reference source and a

Honeywell model 2703 potentiometer. Considerable work was done on the x-y recorder during the course of experimentation, making sure that it was linear and working properly. The accuracy of the thermocouple was checked by comparison with several reliable thermometers in the temperature range from $0^{\circ}C$ to the boiling point of water and no discreptancy was found.

The areas under the thermoluminescence glow curves were integrated using a model 39231 planimeter from Gelman Instrument Company. The areas, in units of intensity per millivolt, were converted to intensity per $^{\circ}C$ using a conversion factor obtained by the "least squares" method. Data from the National Bureau of Standards calibration chart was fed into a computer program to obtain this conversion factor.

All least squares calculations were done by the IBM model 360-75 computer located at TUCC in Durham, North Carolina. Access to the computer was gained through a series 33 teletype terminal from ComData Corporation, located on the campus of UNC-G. The CPS program LINREG from the public library at TUCC was the program used for all the least squares calculations.

Experimental Problems With the Equipment

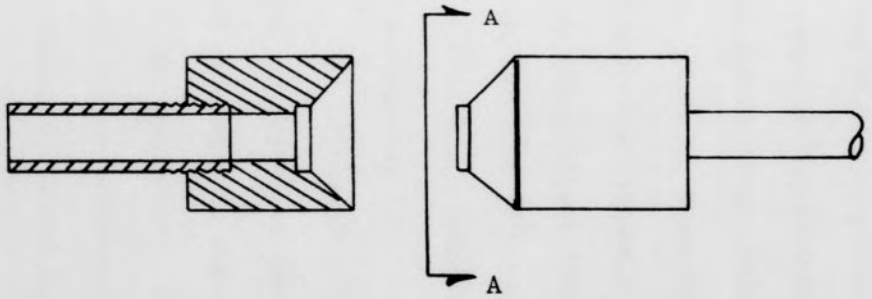
Although most of the experimental equipment was already set up it was necessary to solve several experimental problems before reliable data were taken. The most important problems were shielding the crystal from visible light, measuring the temperature of the crystal accurately while making a glow curve, making sure that the soldering iron was heating at a constant rate, and insuring reproducible geometry.

The crystal was exposed to a minimum amount of visible light between coloration and thermal bleaching to prevent formation of F', M,and R

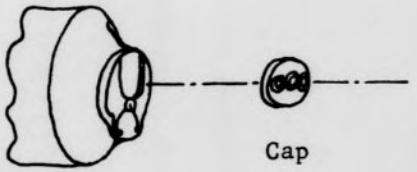
centers which are all aggregates of F centers. Since the thermoluminescence intensity was very small, even after amplification by the phototube, the crystal and phototube had to be completely shielded from outside light while the glow curves were being made. This was accomplished by machining two circular interlocking pieces of asbestos (see Figure 6, Detail A) to fit on the end of the soldering iron and mounting then on the end of the phototube assembly. A clamp was fastened around the coupled apparatus and aluminum foil wrapped around the outside to keep light out while making a glow curve.

In order to measure the temperature of the glow peaks accurately it was necessary to have one end of the thermocouple either touching or very near the crystal as it was being heated. Since it was found impractical to have the end of the thermocouple touching the crystal, several designs were tried before a satisfactory one was chosen. Two grooves were machined, on the tip of the soldering iron, at an angle such that they met just below the crystal. The ends of the copper and constantan wires were silver soldered, placed in these grooves and inserted through two holes drilled in the piece of asbestos fastened to the soldering iron. A cap to hold the thermocouple wires and the crystal in place was made by cutting a section off the tip of the soldering iron and machining holes for screws and a hole through the center of the cap to allow light from the crystal to reach the phototube.

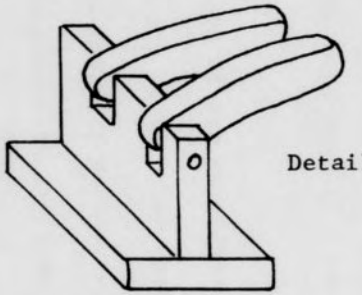
To allow removal of the soldering iron for mounting on the x-ray machine and for the use of a duplicate soldering iron the wires were cut



Detail A: Light shielding apparatus



Section AA: View of soldering tip with cap



Detail B: Plexiglass pressure switch

Figure 6: Details of light shielding apparatus, soldering iron tip, and pressure switch.

and a Plexiglass pressure switch was made to connect the wires of the thermocouple (see Figure 6, Detail B).

The thermoluminescence theory presented in the second chapter assumed a constant heating rate and much care was taken to insure that the glow curves were made at a constant heating rate. The heating rate was varied by adjusting the input voltage to the soldering iron with a Staco model 3PN 1010 variable autotransformer. A fast enough heating rate was chosen to produce sharp peaks and to be linear through the temperature range of the glow peaks, yet slow enough to heat the crystal uniformly and to assure that the thermocouple was at the same temperature as the crystal. The heat conducting efficiency of the soldering iron was improved by making a new tip out of a piece of copper tubing and the ends of the original solid tip. The heating rate used for most of the data varied from 36^{o}C per minute to 38^{o}C per minute; some of the earliest data was taken using a heating rate from 17^{o}C per minute to 18^{o}C per minute.

One of the essential requirements of any experimental work is the ability to reproduce data. To relate any of the glow curves meaningfully it was necessary to reproduce the same geometry at the x-ray machine and at the phototube. The crystal was placed at the same position on the tip of the soldering iron by cutting a rectangular slit on the tip (see Figure 6, Detail A, Section AA). The asbestos coupling was designed in a manner such that as the pieces fit tightly the crystal would be the same distance away from the window of the phototube (see Figure 6, Detail A). Grooves were filed on the pieces of the asbestos coupling so that the

crystal was placed with the same orientation in front of the phototube window (see Figure 5, Detail A). A piece of lead shielding was machined on one side so that it could be attached to the x-ray port. A hole was machined in the other side allowing the tip of the soldering iron, containing the crystal to be placed the same distance away from the x-ray port each time. By carefully placing the soldering iron in a clamp the crystal was placed at the same orientation in front of the x-ray port.

Two 6199 phototubes were used during the course of experimentation. Unfortunately, the second tube was not purchased until much of the experimental work had been done. This second phototube had approximately one hundred times less dark current than the original phototube. The new tube made it possible to make glow curves on a more sensitive scale and also, to determine the thermoluminescence emission spectrum.

Experimental Problems with the Crystals

The theory discussed in the second chapter was for a single isolated glow curve. Individual glow curves were isolated by thermal bleaching, by optical bleaching and by varying the x-ray exposure time. When two glow peaks were overlapping the low temperature peak was bleached out thermally by heating the crystal to the peak temperature of the lower temperature peak, allowing the crystal to cool and then reheating the crystal to produce a single isolated glow peak. A single isolated high temperature peak was made by illuminating the colored crystal with green light corresponding to the maximum F band absorption.

Since the higher temperature peaks only appeared after longer x-ray exposure times, the low temperature peaks were isolated by exposing the crystal for short periods of time.

The correct scale for making individual glow curves was chosen by trial and error. The sensitivity of the electrometer and the y-axis of the x-y recorder were varied to allow the thermoluminescence intensity to cover as much of the graph paper as possible without amplifying the noise too much. More accurate area measurements were made by choosing the scales in this manner.

Some of the crystals were heated in an oven to 400^{o}C, for varying periods of time up to 24 hours, to ascertain the effects of heat treatment. Some of the heated crystals were fast quenched (cooled quickly to room temperature) and some were slow quenched (cooled more slowly over a period of several hours).

CHAPTER 4

EXPERIMENTAL RESULTS AND CONCLUSIONS

Six KCl crystals were x-irradiated for purposes of making thermoluminescence glow curves. One was obtained from a group of optically polished crystals purchased from Harshaw Chemical Company. The other 5 crystals were cleaved from a single KCl crystal grown at Oak Ridge National Laboratory (ORNL). This crystal was part of Boule number 03076 grown by C. T. Butler of the Solid State Division and was secured through the courtesy of Dr. J. A. Crawford of the University of North Carolina at Chapel Hill. Equipment to test the relative purity of the ORNL crystals was not available. However, according to information given by Dr. Crawford these crystals are the purest grown to date. The ORNL crystals were named in sequence KCl-1 to KCl-5 and the Harshaw crystal was designated as KCl-6. All of the crystals were rectangular sections about 5 x 6 $mm.^2$ and ranged in thickness from .69 to 1 mm.

Some of the crystals, KCl-2, KCl-3, and KCl-5, were subjected to heat treatment in order to determine the effects of heating on their glow curves. KCl-2 was heated in an oven at 400°C for periods of 2, 4, 17, and 24 hours then fast quenched. The crystal was x-rayed for periods of one hour using the same beam current and a glow curve was made between each phase of heat treatment. KCl-3 was baked in the oven at 400°C for the same periods of time and slow quenched. These glow curves for KCl-2 and KCl-3 were then analyzed qualitatively to ascertain the effects of heat treatment and to compare the

methods of fast and slow quenching. Also, KC1-5 was heated at 400°C for periods of 6, 8, 17, and 24 hours then fast quenched and KC1-6 was heated for 24 hours at 400°C then fast quenched. Crystals of KC1-1 and KC1-4 were not subjected to any heat treatment.

The Effects of Heat Treatment

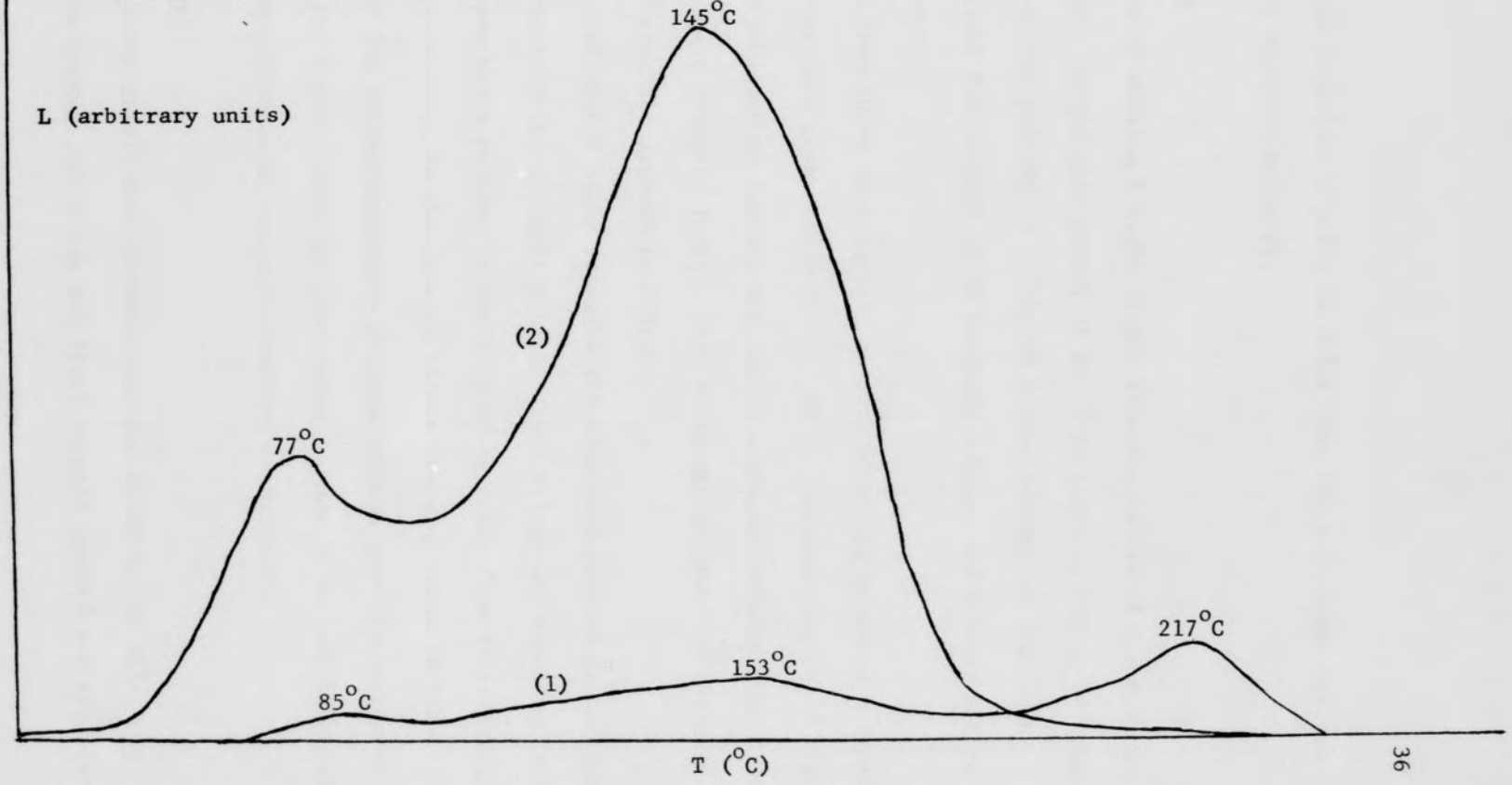
The glow curves of all of the crystals, with the exception of KC1-1, contained more than one glow peak. The qualitative effects of heat treatment on glow curves of KC1-2 is shown in Figure 7.

As is seen by observing these glow curves, the overall effect of heat treatment was to reduce the high temperature peak and to increase the low temperature peaks. Similar effects were observed on the glow curves of KC1-3 and KC1-5. The lowest temperature peaks are thought to be a result of some type of impurity and the highest temperature peak a result of internal stress within the crystal. The a proposed explanation of the effects of heat treatment is that the impurity traps and F center traps are some how narrowed by heating the crystal. If this is true, then the thermoluminescence intensity of these lower temperature peaks would be increased for a given heating rate beacuse the traps are being emptied at a higher rate as a result of the smaller energy range for each glow peak. The effect of heat treatment on the high temperature peak is explained if the strain was annealed out by heating. Then, intensity of the high temperature peak is decreased because not as many traps are available to contribute to the glow peak. As soon as the above effects of heat treatment were observed it was considered as a possible means of isolating the lower temperature F center peaks by

Figure 7: Glow curves of KC1-2 showing the effects of heat treatment.

Curve 1: Made after 1 hr. x-irradiation before heat treatment.

Curve 2: Made after 1 hr. x-irradiation and 17 hr. of heat treatment.



decreasing the high temperature peaks in order that the area under the low temperature curves might be measured.

Optical Bleaching

The effects of shining F light (light from the center of the F band absorption spectrum) on the glow curves of KCl-2 is shown in Figure 8. The crystal was x-rayed for periods of 1 hour at a beam current of 20mA then bleached with F light for periods of 30 minutes, 1 hour, and 5 hours before making the glow curves.

As is seen from these glow curves, optical bleaching produced a single isolated high temperature peak around 200°C. It is believed that the F light empties the lower temperature centers and leaves a single isolated center corresponding to the deepest trapping level. This trend was observed in the glow curves of all the crystals exposed to F light.

It is believed that F light releases the electrons trapped in the low temperature centers into the conduction band. This allows the electron to recombine with trapped holes present in the colored crystal, thus determining the number of holes present in the crystal before the glow curve is made. Since the order of the thermoluminscence process depends upon the number of holes present in the crystal when the glow curve is made it is possible that the order might be controlled using optical bleaching techniques.

Typical Glow Curves

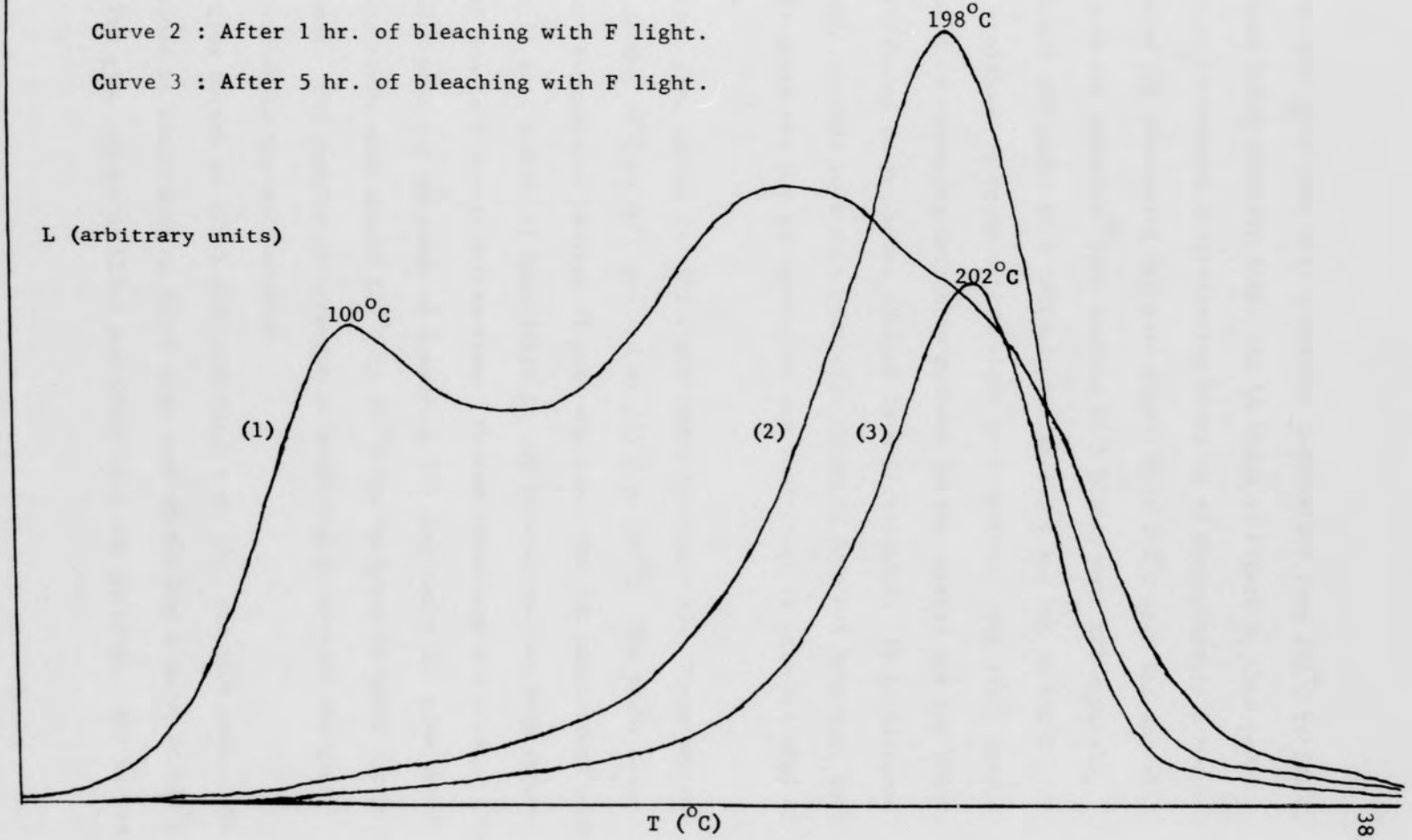
The glow curves of all the crystals with the exception of KCl-1 contained several glow peaks. KCl-1 was the first crystal cleaved and exhibited

Figure 8 : Glow curves of KC1-2 showing the effects of optical bleaching.

Curve 1 : No optical bleaching.

Curve 2 : After 1 hr. of bleaching with F light.

Curve 3 : After 5 hr. of bleaching with F light.



a single isolated glow peak with a maximum temperature from 155°C to 170°C, depending upon x-ray exposure time. As is shown in Figure 9, this peak increased with increasing x-irradiation times up to approximately 8 hours then saturated for increasing exposure time. This 165°C peak was not observed by Jain and Mehendru[9] when working with highly pure KCl crystals. They attributed two peaks to F centers, one at 135°C and one at 190°C which were explained in terms of two kinds of F centers. The 135°C peak was attributed to vacancies initially present in the crystal and the 190°C peak was attributed to vacancies created by x-irradiation. It is believed that the ORNL crystals were more pure than those of Jain and Mehendru, that one of their peaks was due to impurities and that there is only one kind of an F center.

Typical glow curves for KCl-2 are shown in Figure 10. There are two peaks, one around 70°C to 80°C and one at 165°C to 170°C. The peaks occur at different temperatures because of some overlap. The low temperature peak is believed to be a result of impurities in the crystal and the high temperature peak due to F center destruction. Thermal bleaching was used to isolate the 168°C peak for purposes of measuring the area under the glow curve. The low temperature peak around 120°C to 140°C was isolated by short x-ray exposure times. The results of attempts at measuring activation energies will be presented in the next section.

The glow curves of KCl-5 also contained more than one glow peak. The same techniques as those used on KCl-2 were used to isolate a curve at 110°C to 120°C. The glow curves of KCl-4 and KCl-6 were not analyzed. The curves

Figure 9 : Glow curve of KCl-1 showing single isolated peak.

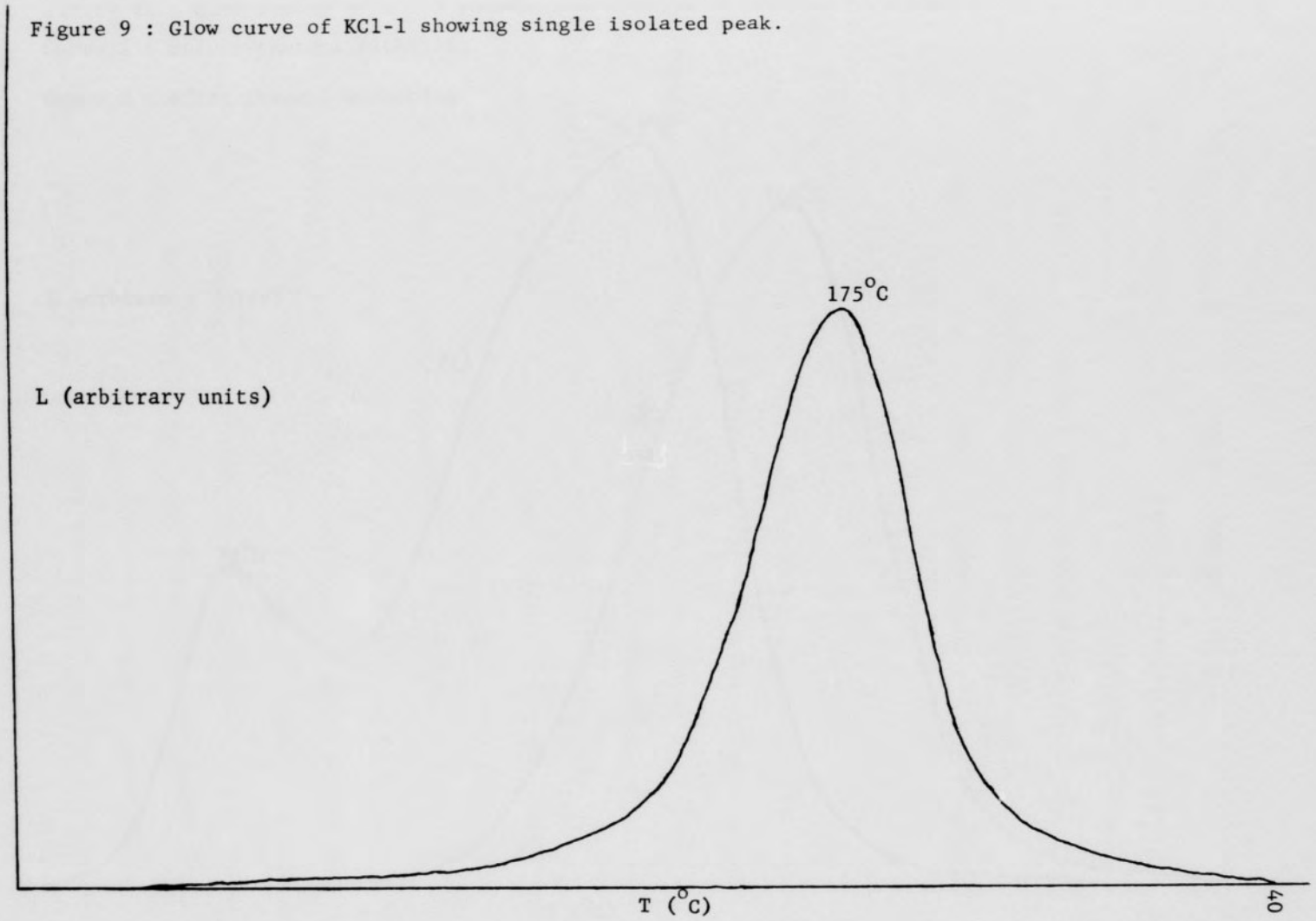
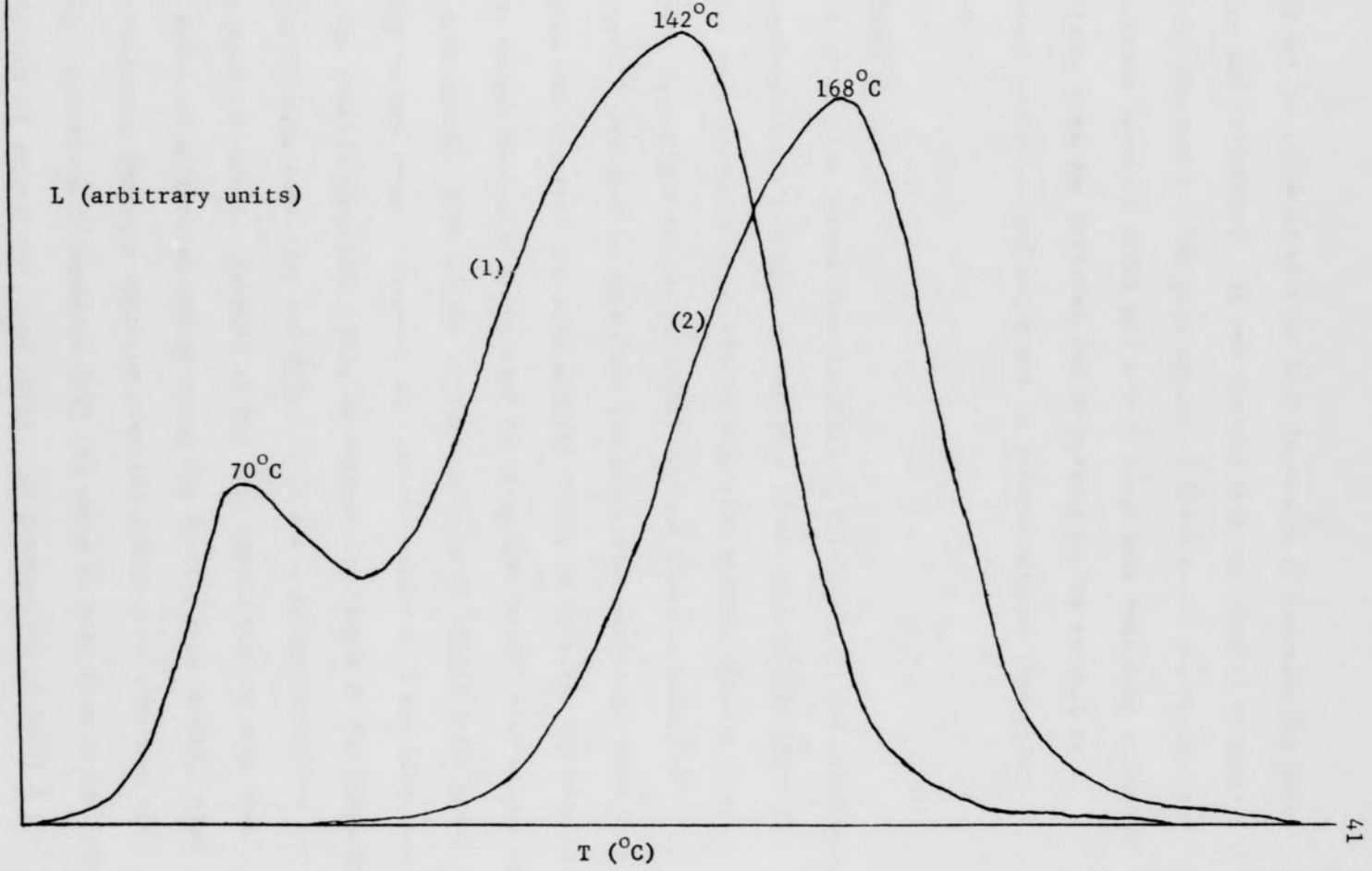


Figure 10 : Glow curves of KCl-2 showing the effects of thermal bleaching.

Curve 1 : Before thermal bleaching.

Curve 2 : After thermal bleaching.



of KCl-4 could not be isolated without heat treatment to increase the peaks above the noise and background. It was desired that one crystal be kept without any heat treatment. The glow curves of KCl-6 could not be analyzed because of numerous impurity peaks and a very large peak beginning at around 250°C. This large peak was believed due to strains in the crystal as a result of optical polishing and could not be reduced without significant heat treatment.

Activation Energies

A total of 42 glow curves from crystals of KCl-1, KCl-2, and KCl-5 were analyzed. Whenever it was possible to obtain a clean leading edge the activation energies were measured using the initial rise method. Also a first order expression equivalent to equation (40) derived from the theory of Kelly and Laubitz[12] was used to calculate the activation energies. When very little agreement was observed the more general theory of Halperin was adopted. Table 1 shows an estimation of K obtained by using the initial rise values of the activation energies. Some of the curves appear to be nearly first order and some nearly second order. However, some of the values of K are less than one and some are greater than two. This is outside the limits of the Halperin model according to equations (38) and (39). This was a disappointing but not completely unexpected result. Several of the glow curves yielded more than one possible value of activation energy using the initial rise method. Also the thermoluminescence emission spectrum revealed evidence of more than one energy present. According to equation (32) the range of r is from .5 to .368 between the limits of second and first order. An examination of Table 1

Table 1: Tabulated results of analyzed glow curves.

Crystal	Curve	Exposure Time in Hours	T_p, ^oK	Q_p	E, Initial Rise, eV	r	K	R, $^oK^{-1}$
KC1-1 *	7	8.25	437	.056	1.33	.473	1.34	11.53
	8	10.00	440	.052	1.45	.453	1.26	13.12
	9	25.66	448	.059	1.30	.445	1.24	11.57
	** 10	5.00	434	.087	.85	.505	1.46	9.78
	11	12.00	440	.057	1.31	.471	1.20	12.46
	** 12	6.00	435	.088	.94	.495	1.42	11.03
	** 13	14.00	439	.069	1.09	.466	1.30	10.55
	** 14	24.00	441	.100	.74	.506	1.47	9.82
KC1-2	22	1.50	441	.064	1.18	.385	1.29	10.41
	24	11.50	435	.065	1.15	.529	1.90	7.06
	25	6.00	439	.074	1.02	.467	1.40	8.37
KC1-5	23	.33	373	.044	1.47	.604	2.66	8.77
	30	.17	397	.057	1.20	.536	1.77	9.47
	33	.08	394	.059	1.08	.565	1.80	8.54
	34	.17	395	.068	1.26	.592	2.22	8.04
	35	.25	377	.052	1.25	.593	2.07	9.37
	36	.25	386	.052	1.28	.591	2.16	8.77
	37	.17	392	.056	1.20	.549	1.81	9.52
	38	.50	401	.060	1.15	.550	1.92	7.87
	41	1.00	483	.085	.97	.389	.99	9.25

*The heating rate for the KC1-1 curves was approximately one-half that of the other curves.

**Used a beam current of 15 mA, all other curves used a beam current of 20 mA.

shows that r exceeds the limits when K exceeds the first and second order limits in several cases. The above results indicate that the Halperin model does not apply to all of the glow curves. A more reliable test would be to find K using equation (32), however, after considerable effort, it was found that a value of K using equation (32) could only be obtained by a computer program to approximate K to the desired accuracy. Since it is believed that the Halperin model does not apply to all of the glow curves and due to a limited amount of time, a computer evaluation of K was not attempted.

Emission Spectra

The thermoluminescence emission spectra of several crystals including others than those used for making glow curves were analyzed during the latter part of experimentation. It was observed that the heat treated crystals had a narrow emission spectrum with definite structure and that the emission spectrum of crystals with no heat treatment exhibited a broader spectrum with no apparent structure. The intensity of the spectra of the heat treated crystals was greater, permitting a better resolution of the energies with the monochromator. All of the glow peaks had essentially the same emission spectra regardless of their peak temperature. Three energies of 2.33, 2.65, and 2.94 electron volts were observed corresponding to wavelengths of 5300, 4650, and 4200 angstroms. It is believed that a more conclusive picture of thermoluminescence would have been obtained had it been possible to measure the emission spectra of all of the crystals which were used to make the glow curves analyzed. This was not possible because three of the crystals were damaged before a more sensitive phototube was obtained.

Optical absorption measurements were made and the characteristic F band absorption was observed in all cases. Also, there was some evidence of hole centers present in the absorption band of some of the crystals. The F band was decreased by exposing the crystals to F light between absorption runs. Equation (1) was used to estimate the number of F centers present for a typical optical absorption curve and found to be $.74 \times 10^{17}$ F centers per $cm.^3$.

Summary

The effects of heat treatment and optical bleaching on the glow curves of highly pure KCl crystals were studied. It was found that heat treatment increased the low temperature glow peaks and decreased the highest temperature peak. It was proposed that these effects were a result of narrowing the energy trapping levels and of annealing out the strains in the crystals. Optical absorption decreased the low temperature peaks creating a single high temperature glow peak. It is believed that this was a result of optically destroying the low temperature centers before the glow curve was made.

All of the glow curves, with the exception of those for one crystal, exhibited more than one glow peak. In all of the glow curves made, a glow peak appeared around $160^{\circ}C$ to $170^{\circ}C$ and was attributed to the destruction of F centers. This result was contrary to previous experimenters[10] and believed to be a result of having more highly pure crystals. No evidence was found to indicate the presence of more than one kind of F center.

The Halperin model developed assumed that only one trapping level and one hole level were responsible for the thermoluminescence of a single glow peak. It is believed that more than one level is responsible for a single

glow peak in KCl as indicated by the emission spectra. Also, it is proposed that the data does not agree with the Halperin model because of the multiple energy level result and that an even more general model is needed which would take into account more than one hole level.

The thermoluminescence emission spectrum was measured and found to be more intense, narrower, and to possess a more definite structure in the heat treated crystals. It was proposed that these effects were a consequence of narrowing the energy levels as a result of heating the crystal. An over all observation indicated that thermoluminescence was neither first order or second order but somewhere in between in general.

Finally, optical absorption measurements were made which indicated that F centers were produced by x-irradiation and that F center destruction gives rise to thermoluminescence.

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